

Vibrational spectra and analysis of 2-methyl para benzoquinone

E James Jebaseelan Samuel¹ and S Mohan^{2*}

¹ Vellore Institute of Technology (Deemed University), Vellore-632 014, India

² Faculty of Applied Sciences, Department of Materials Science,
Asian Institute of Medicine, Science & Technology,
08000 Sungai Petani, Amanjaya, Kedah, Malaysia

E-mail : s_mohan@lycos.com

Received 30 December 2002, accepted 12 July 2003

Abstract . The FTIR and FT Raman spectra of 2-methyl para benzoquinone have been recorded. The observed frequencies were assigned to various modes of vibrations on the basis of normal coordinate calculations, assuming C_s point group symmetry. The potential energy distribution associated with each normal mode was also reported. The assignment of fundamental vibrations agree well with the calculated frequencies.

Keywords FTIR Spectra, FT-Raman spectra, 2-methyl para benzoquinone, force field, vibrational analysis

PACS No. 33.20.Ea, 33.20.Fb, 33.20.Tp, 78.30.Cp

Quinones play important role in electron transfer in bacteria [1] photosystems of green plants [2] and mitochondria [3]. It is used as a chemical intermediate, a polymerization inhibitor, an oxidizing agent, a photographic chemical, a tanning agent and a chemical reagent [4]. Benzoquinones find applications as oxidants, bactericides and chemical intermediates [5]. 1,4-Benzoquinone is also used as an intermediate in the preparation of hydroquinone, which is important in the photographic and dye industries and is used in the tanning of leather [6]. The vibrations of p-benzoquinone were studied by several authors [7-11]. Nonella [12] studied the structure and harmonic force fields of 2-methyl-1,4-benzoquinone and Alegria *et al* [13] studied the photolyses of phosphate buffered air and nitrogen-saturated solutions containing the water-soluble quinones like 2-methyl-1,4-benzoquinone. Trivi *et al* [14] found that 2-methyl-1,4-benzoquinone are readily reduced by d-glucose in the presence of glucose oxidase. In spite of its considerable importance in different fields, the spectra of these molecules are not investigated in detail. To the best of our knowledge, a complete vibrational analysis of 2 methyl-para benzoquinone (2MPBQ) is not available in the literature. The present investigation of the above compound has been undertaken for the first time. Here, we have analysed the nature of normal

vibrations of the molecule through FTIR and FTR spectra and presented the potential energy distribution.

The sample of 2MPBQ was obtained commercially from M/s.Fluka Chemicals, Switzerland with a stated purity of greater than 98% and it was used as such without further purification. The Raman spectrum in the range of 3500-50 cm^{-1} was recorded on a Bruker model IFS 66 interferometer equipped with a model FRA 106 FT Raman module accessory. The IR spectrum of the sample was recorded in the solid phase using the same instrument in the range of 4000-400 cm^{-1} . The data were recorded to the coaddition of 32 scans at $\pm 2 \text{ cm}^{-1}$ resolution with 200 mW of power at the sample in both techniques.

Wilson's F-G matrix method was used in an attempt to study the normal coordinate analysis [15-17]. The molecule under investigation, has planar structure and belongs to C_s point group symmetry. For a C_s symmetry, the 39 fundamental vibrations fall into 27 in-plane vibrations of the a' species and 12 out-of-plane vibrations of a'' species. All the vibrations are both infrared and Raman active. In the present work, both in-plane and out-of-plane vibrations are treated completely. The structural parameters employed in the present work are taken from Sutton's table [18]. The normal coordinate calculations were performed using the program developed by Fuhrer *et al* [19], after suitable modification in our laboratory. Internal

* Corresponding Author

coordinates for the out-of-plane vibrations are defined as recommended by IUPAC. The simple valence force field is adopted for both in-plane and out-of-plane vibrations.

The observed infrared and Raman frequencies and the calculated frequencies along with the percentage PED (Potential Energy Distribution) of various modes of vibration of 2MPBQ are presented in Table 1. The recorded FTIR and FT Raman spectra of 2MPBQ are shown in Figures 1 and 2 respectively.

C-H vibrations :

In aromatic rings, the C-H stretching absorption are usually observed between 3100 and 3000 cm^{-1} [20, 21]. Thus, the absorption band at 3053, 3030, 3000 cm^{-1} are assigned to C-H stretching. These are pure modes and the PED results exhibit that they are around 80%.

The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region 1300-1000 cm^{-1} . In

Table 1. Observed and calculated wavenumbers (cm^{-1}) and potential energy distribution (PED) for 2 Methyl-P-Benzoquinone

Species	Observed frequency/Int		Calculated	Assignment	% PED
	FTIR	FTR	wave number		
-	3318 m	-	-	2 x 1662	-
-	3260 s	-	-	1662 + 1600	-
-	-	3080 vw	-	1643 + 1443	-
-	-	3060 m	-	1662 + 1392	-
a'	3053 s	-	3047	CH stretching	81 ν_{CH}
a'	-	3030 m	3021	CH stretching	74 ν_{CH}
a'	3000 m	3001 vw	3000	CH stretching	88 ν_{CH}
a'	-	2966 vw	2961	CH asymmetric stretching in CH_3	90 ν_{asCH}
a''	2960 s	-	2953	CH asymmetric stretching in CH_3	89 ν_{asCH}
a'	-	2929 m	2926	CH symmetric stretching in CH_3	83 ν_{sCH}
-	2920 w	-	-	1580 + 1346	-
-	2887 vw	-	-	1600 + 1287	-
-	2573 w	-	-	2 x 1287	-
-	2533 vw	-	-	1232 + 1299	-
-	2447 vw	-	-	1299 + 1140	-
-	2373 vw	-	-	3053 - 680	-
-	2273 vw	-	-	2960 - 680	-
-	2153 w	-	-	1662 + 486	-
-	2020 w	-	-	3053 - 1033	-
-	1967 vw	-	-	3053 - 1086	-
-	1933 vw	-	-	2960 - 1033	-
-	1847 vw	-	-	2 x 920	-
-	1827 vw	-	-	2960 - 1140	-
-	1786 w	-	-	1346 + 441	-
-	-	1772 vw	-	2 x 886	-
-	1746 m	-	-	920 + 822	-
a'	1662 vs	1662 vs	1660	C=O stretching	74 $\nu_{C=O}$ + 16 ν_{CC}
a'	-	1643 m	1639	C=O stretching	88 $\nu_{C=O}$
a'	-	1615 vw	1611	C=C stretching	81 $\nu_{C=C}$ + 10 ν_{CH}
a'	1600 s	1600 w	1594	C=C stretching	92 $\nu_{C=C}$
a'	1580 m	-	1573	C-C stretching	71 ν_{C-C} + 16 $\nu_{C=O}$
a'	-	1443 vw	1439	CH_3 asymmetric deformation	74 δ_{asCH} + 11 δ_{C-CH_3}
a'	1425 vs	1426 vw	1421	CH_3 symmetric deformation	89 δ_{sCH}
a'	-	1392 m	1386	C- CH_3 stretching	71 ν_{C-CH_3} + 13 ν_{C-C}
a'	1373 m	-	1368	C-C stretching	80 ν_{C-C}
a'	-	1353 m	1350	C-C stretching	91 ν_{C-C}

a'	1346 s	-	1341	C-C stretching	$89 \nu_{C-C}$
a'	1299 s	1300 vw	1291	C-H in plane bending	$74 \beta_{CH} + 10 \beta_{C-H_0}$
a'	1287 m	1280 vw	1282	C-H in plane bending	$69 \beta_{CH} + 23 \beta_{CH}$
a'	1232 m	1232 m	1226	C-H in plane bending	$84 \beta_{CH}$
a''	1140 s	1140 w	1131	CH ₃ wagging	$69 \omega_{CH} + 28 \tau_{CH}$
a''	1086 m	1091 m	1084	CH ₃ twisting	$59 \tau_{CH} + 32 \omega_{CH}$
a''	1033 m	1033 vw	1027	C-H out of plane bending	$56 \eta_{CH}$
a''	1000 s	-	989	C-H out of plane bending	$74 \eta_{CH}$
a''	-	966 vw	961	C-H out of plane bending	$61 \eta_{CH} + 28 \eta_{CCC}$
a'	-	927 vw	919	CCC in plane bending	$86 \beta_{CCC} + 12 \beta_{C-H_0}$
a'	920 s	-	911	CH ₃ rocking	$66 \rho_{CH_3} + 20 \delta_{CH_3}$
a'	-	886 vw	880	CCC in plane bending	$74 \beta_{CCC}$
a'	882 s	-	874	CCC in plane bending	$66 \beta_{CCC} + 12 \beta_{CH}$
a'	853 w	-	848	CCC in plane bending	$72 \beta_{CCC} + 26 \beta_{CH}$
a'	822 m	826 vw	821	CCC in plane bending	$86 \beta_{CCC}$
a''	-	800 vw	792	CCC out of plane bending	$72 \eta_{CCC} + 19 \eta_{CH}$
a''	760 vw	-	752	CCC out of plane bending	$49 \eta_{CCC} + 22 \eta_{CCC} + 12 \eta_{CH}$
a''	680 m	680 w	673	CCC out of plane bending	$54 \eta_{CCC} + 26 \eta_{CH}$
a''	585 vw	580 vw	581	CCC out of plane bending	$68 \eta_{CCC} + 19 \eta_{C-H_0}$
a'	486 vw	482 vw	480	C=O in plane bending	$74 \beta_{C=O} + 12 \beta_{CCC}$
a'	-	453 vw	446	C=O in plane bending	$79 \beta_{C=O} + 14 \beta_{CCC}$
a''	441 s	-	430	C=O out of plane bending	$68 \eta_{C=O} + 20 \eta_{CCC}$
a''	404 vs	-	397	C=O out of plane bending	$71 \eta_{C=O} + 21 \eta_{CCC}$

vs- very strong, s- strong, m- medium, w- weak, vw- very weak, v- stretching, δ - deformation, β - in-plane bending, η - out-of-plane bending, ρ - rocking, ω - wagging and τ - twisting/torsion

2MPBQ, the C-H in-plane bending is assigned to 1299, 1287 and 1232 cm⁻¹. The C-H out-of-plane bending modes are assigned to 1033, 1000 and 966 cm⁻¹.

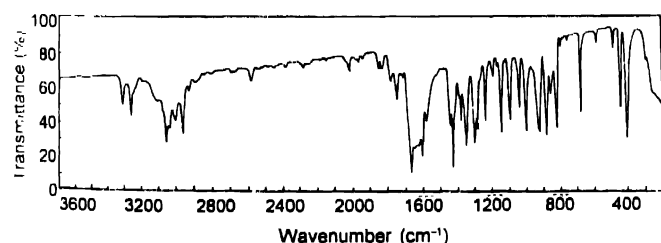


Figure 1. FTIR spectrum of 2-Methyl -p- Benzoquinone.

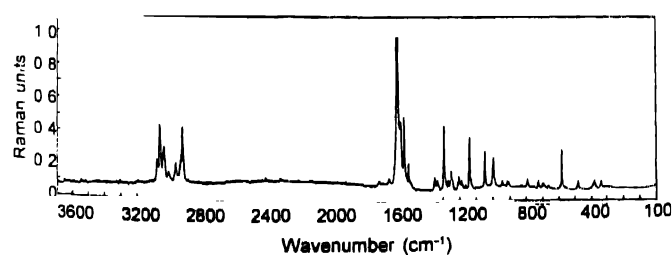


Figure 2. FT-Raman spectrum of 2-Methyl-p benzoquinone.

Carbon vibrations :

The carbon stretching modes are expected in the range from 1650 to 1400 cm⁻¹. The C=C stretching of 2MPBQ is found in the Raman spectrum at 1615 cm⁻¹ and at 1600 cm⁻¹. The C-C stretching modes are assigned to the bands at 1580, 1373, 1353 and 1346 cm⁻¹. These frequencies appear in the respective range and the PED confirms these results and further shows that these modes are pure.

The in-plane carbon bending vibration are obtained from the non-degenerate band at 1010 cm⁻¹ (b_{1u}) and degenerate modes at 606 cm⁻¹ (e_{2g}) of benzene. In the present work, the bands occurring at 920, 882, 853 and 822 cm⁻¹ in IR and 927, 886 and 826 cm⁻¹ in Raman spectra are assigned to the CCC in-plane bending.

Similarly, the CCC out-of-plane bending modes are defined with reference to 703 cm⁻¹ (b_{2g}) and degenerate 404 cm⁻¹ (e_{2u}) modes of benzene. The CCC out-of-plane bending modes of 2MPBQ under C_s symmetry is attributed to Raman frequencies observed at 800, 680 and 580 cm⁻¹ and 760, 680 and 585 cm⁻¹ in IR. Both the in-plane and out-of-plane vibrations are described as mixed modes as there are about 20% PED contribution mainly

from C-H in-plane bending and out-of-plane bending vibrations respectively.

Carbonyl group vibrations :

In the case of paraquinones, either one or two carbonyl absorption bands may be observed. The range being 1690-1655 cm^{-1} [22, 23]. In 2MPBQ, C=O stretching occurs at 1662 and 1643 cm^{-1} of Raman.

The C=O in-plane bending mode is assigned to 482, 453 cm^{-1} in Raman and C=O out-of-plane bending mode is assigned to 441 and 404 cm^{-1} of IR.

Methyl group vibrations :

In 2MPBQ, one expects 3 distinct bands for each molecule in the region 2900 to 3000 cm^{-1} and these can be assigned to the stretching vibrations of CH_3 group. According to the normal coordinate analysis, the two asymmetric modes of CH_3 are attributed to 2966 cm^{-1} and 2960 cm^{-1} and 2929 cm^{-1} is assigned to symmetric stretching. These assignments are confirmed by PED which contributes above 85%.

The deformation modes of methyl group are observed in the region 900 to 1500 cm^{-1} . The CH_3 asymmetric and symmetric deformations are identified at 1443 cm^{-1} and 1426 cm^{-1} respectively. The CH_3 wagging, twisting and rocking modes are assigned to 1140 cm^{-1} , 1086 cm^{-1} and 920 cm^{-1} respectively. The C- CH_3 stretching in this molecule is observed at 1392 cm^{-1} .

The remaining observed frequencies in Table 1 may be accounted for from allowed combinations and overtones and fundamentals, which give additional support for their allocations.

The potential energy distribution associated with each vibrational mode has been calculated using the relation in order to check whether the chosen set of vibrational frequencies contributes the maximum.

$$PED = \frac{F_{ii} L_{ik}^2}{\lambda_k}$$

where F_{ii} are the force constants defined by damped least square technique, L_{ik} the normalised amplitude of the associated element (i, k) and λ_k the eigen value corresponding to the vibrational frequency of the element k. Table 1 gives the potential energy to each normal modes and degree of mixing of other modes.

Thus, in the present work, a complete vibrational

assignments and analysis have been performed for 2-methyl-para-benzoquinone on the basis of normal coordinate calculations using the FTIR and FT Raman spectra.

Acknowledgment

The authors are thankful to the learned referee for his valuable comments which improved the paper to the present form.

References

- [1] M Y Okamura and G Feher *Adv. Photosynth* **2** p577 (1995)
- [2] W Maentele and M Peirard *Nonlinear Excitations in Biomolecules* (Berlin : Springer) p295 (1995)
- [3] H Nohl, L Gille and K Strariek *Ann. N.Y. Acad. Sci.* **854** p394 (1998)
- [4] *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man* **15** (1977)
- [5] Kirk-Othmer *Encyclopedia of Chemical Technology* (New York : John Wiley) (1980)
- [6] *Ullmann's Encyclopedia of Industrial Chemistry* Sixth edn A3 p573 (2001)
- [7] M Nonella and P Tavan *Chem. Phys.* **19** 199 (1995)
- [8] S E Boesch and R A Wheelles *J. Phys. Chem.* **99** 8125 (1995)
- [9] Y Yamakita and M Tasumi *J. Phys. Chem.* **99** 8524 (1995)
- [10] W J Barreto, D A M Zaira and L F C De Oliveira *Spectrochim. Acta* **50A** 1031 (1994)
- [11] R S Mock and E D Grimsrud *J. Phys. Chem.* **94** 3550 (1990)
- [12] M Nonella *J. Phys. Chem.* **100** 20148 (1996)
- [13] Antonio E Alegria, Amaris Ferrer and Elsa Sepulveda, *Photochem. and Photobiol.* **66** 436 (1997)
- [14] Svetlana Triva, Vladimir Laskovac, Jasmina Zeremski, Miroslav Vrvic and Gary W Winston *Bioorganic Chem.* **30** 95 (2002)
- [15] E B Wilson Jr *J. Chem. Phys.* **7** 1047 (1939)
- [16] E B Wilson Jr *J. Chem. Phys.* **9** 76 (1941)
- [17] E B Wilson Jr, J C Decius and P C Cross *Molecular Vibrations* (New York : McGraw-Hill) (1955)
- [18] L E Sutton *The Interatomic Bond Distances and Bond angles in Molecules and Ions* (London : London Chem. Soc.) (1983)
- [19] H Fuhrer, V B Kartha, K L Kidd, P J Kruger and H H Mantsch, *Computer Program for Infrared and Spectrometry, Normal Coordinate analysis* Vol. 5 (Ottawa, Canada : National Research Council) (1976)
- [20] G Varsanyi *Assignments for vibrational spectra of seven hundred benzene derivatives* Vol. I (London : Adam Hilger) (1974)
- [21] W O George, P S McIntyre *Infrared Spectroscopy* (New York : John Wiley) (1987)
- [22] C Brian Smith *Infrared Spectral Interpretation* (New York : CRC Press) (1999)
- [23] George Socrates *Infrared and Raman Characteristic Group Frequencies* (New York : John Wiley) (2001)